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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

EVALUATION OF MICRO QUANTITIES OF ALUMINUM

by

Julia Flavia Possidoni de Albinati

SUMMARY -- A study was made of the fluorometric procedure used for the determination of microquantities of Aluminum based on the reaction with Pontachrome blue-black-R. Although several papers were written on this subject, lack of agreement was found specially on the influence of certain elements. The operating conditions of the Beckman spectral fluorescence attachment were established, and fluorescent spectra of both reagent and aluminum compound obtained. The optimum wave length for aluminum determination was 605 mμ. The influence of pH, solvent and concentration of the reagent, time of heating, fluorescence stability, etc., were studied and a sensitivity of 0.0001 γ Al/ml was attained. The effect of about 70 different ions was considered and in a next paper a method for the elimination of interference will be discussed.

INTRODUCTION

The ideal analytical identification and evaluation of a given ion in the presence of any other by the use of reagents has not been carried out yet. On the other hand, new and more selective agents have been incorporated repeatedly for analytical purposes. However, when the analysis is associated with unfavorable relations as far as the evaluation of the ion is concerned, namely with interference, the solution becomes more and more complicated.

The purpose of this experiment is to develop a relatively simple process to obtain correct data in the evaluation of micro quantities of aluminum when this ion is in the presence of much larger quantities of any other ion.

For this purpose, the Pontachrome blue-black-R [See note] was used, since it is a reagent which permits the achievement of great sensitivity and, according to the bibliographical information which will be analyzed later, would experience relatively few interferences.

[Note:] Also known as Superchrome-blue-black, Blue au chrome 2R, Blue noir au chrome NR, Blue noir solochrome BS, and appears with the number 202 in the Color Index (CI 202). In this paper we will use the abbreviation CI 202.

In 1937 White and Lowe (1) described for the first time the use of CI 202 as reagent for aluminum. This compound is the sodium salt of the acid 4-sulfo 2-2 dehydroxy-azo-naphtalene. In that paper it was stated that the orange fluorescence characteristic of the complex that aluminum forms with this reagent could experience interference only by certain colored ions and by the fluoride ion, and it was specially recommended for the evaluation of aluminum in the presence of berilium. The influence of acids and alkalis on fluorescence was also indicated. Galium was included among the ions which would not interfere. The sensitivity attained using a mercury lamp as source was 1:5,000,000 (using a 0.1% solution of the reagent).

Later on, in 1941, Bourstyn (2) studied this coloring agent again, mentioning the previous paper and stating the importance of provoking the reaction at the pH at which aluminum hydroxide precipitates. The sodic salt of the reagent was used in a 1% alcoholic solution, and the pH was controlled using an acetate-acetic solution. The author attained a sensitivity of 2×10^{-4}N, which decreases when the fluoride ion is eliminated with boric acid.

In 1944 Weissler and White (3) developed a method for the determination of aluminum in steel, bronze and minerals based on the use of CI 202. In that experiment they studied the influence of pH, time, heating and concentration of the reagent. Interferences were eliminated by electrolysis using a mercury cathode. They also analyzed the fluorescent compound, obtaining a relation Al:CI 202 = 1:2. The sensitivity attained with this method was 1:125,000,000.

Later on, in 1947, Charlot (4) after studying several reagents for the ions of the aluminum group, indicated that CI 202 is one of the most convenient ones. This author worked with an aqueous solution of the reagent (0.01%) and controlled pH with an acetic-acetate solution. The sensitivity attained with the proposed semi-quantitative technique was 0.01 γ of Aluminum per ml. (1:100,000,000). Among the interfering ions the author mentions:

Chrome (III) and uranium (VI): interfere slightly.
Cobalt (II) and molybdenum (VI): interfere considerably.
Nickel (II), copper (II), iron (III), titanium (IV), vanadium (IV) and vanadium (V): stop the reaction.

Iron (II): undesirable because it oxidizes forming iron (III).
Cerium (IV), talium (III), gold (III) and platinum (IV): oxidize
    the coloring agent.
Chromium (IV): undesirable because of its color.
Oxalates and fluorides: must be eliminated before the reaction.
Galium (III): interferes.

Separations are indicated by extracting the cupferrates in ethyl
acetate (galium, iron, etc.) or by precipitation and filtration (gold,
platinum). To eliminate the interference of cobalt, nickel and copper,
the formation of a complex of these ions with cyanide is provoked.

In 1957 Ishibashi and his associates (5) made a new study of the
application of CI 202 to the evaluation of aluminum. After studying the
influence of pH, they considered convenient to provoke the reaction at
pH 4.8. To develop fluorescence they heated the solution in a double
boiler for ten minutes. They suggest adding different volumes of 0.1%
alcoholic solution, according to the amount of aluminum present [See
note]. With the proposed method they detected 0.004 γ of aluminum per
milliliter. In this paper they studied the effects of several ions,
fifteen of them, and established that Ca^{++}, Mg^{++}, Sr^{++}, Be^{++}, In^{+++},
Mn^{++}, F^- and $PO_4 \equiv$ do not interfere with the reaction. Cu^{++}, Ti^{4+} and
Ni^{++} would produce negative errors. Greater negative errors would be
obtained with Co^{++} and VO_3^-. Fe^{+++} should not be present, and its re-
duction to Fe^{++} using hydroxylamine would not eliminate its interference
completely. Ga^{+++} produces positive errors because of its fluorescence.
The fact that in considering the influence of the different ions the
authors have not attained rations of Al: interference better than 1:20
(except for Mg^{++}, where Al:Mg = 1:500) [See note 2] should be taken into
consideration.

[Note:] In the summary of the original paper the use of 1%
aqueous solution of the coloring agent is mentioned, although when refer-
ring to reagents and apparatus, (cap. 2) a 0.1% solution in alcohol is
prepared.

[Note 2:] It is convenient to mention that in the summary of this
paper; C. A. 15.333g (1958) it is mentioned that: "Co^{++}, VO_3^- and large
quantities of Cu, Ti and Ni do not interfere," while in the original
paper it is stated that "the elements Fe^{+++}, Ca, Co and vanadic acid
interfere in the determination of aluminum by this method. Besides,
the presence of large quantities of copper, Ti and Ni has a perturbing
influence."

Contradictions can be found in the summary of the bibliographic
information. Specially important from the analytical point of view are
those related to interference and operating conditions. Therefore, it
was considered convenient:

I. To study the instrumental modifications which would make possible the success of the method.

II. To review the most important variables in the analytical process with the purpose of developing a technique which would permit the achievement of a high degree of sensitivity and the acquisition of reproducible data.

III. To determine the influence of several ions.

IV. To develop fast methods for the elimination of interference.

In the first part of this paper it is described how the first three goals mentioned above were attained.

EXPERIMENTAL PART

A. Apparatus and Reagents:

    a) Spectrophotometer Beckman, model DU, provided with:

        1) attachment for the determination of spectral fluorescence No. 22850, with mercury lamp No. 2260 and Corning filter No. 9863.

        2) attachment for the determination of total fluorescence No. 2980.

        3) normal equipment for absorptiometry in the ultraviolet and visible range.

    b) Beckman pH-meter, Zeromatic model.

    c) Controlled pipettes and matrasses.

    d) Silica precipitation glasses.

    e) Silica distillation apparatus with polished junctions.

    f) Drugs: salts, acids, solvents, etc., of good quality "for analysis" or "spectroscopically pure."

    g) The CI 202 used was kindly given by the Duperial company.

B. Solutions

In every case deionised water obtained with a "DESTILIT" mixed bed demineraliser was used.

All the solutions prepared for this experiment were preserved in a polythene container, to avoid possible contaminations with aluminum from glass (specially in case of acid solutions).

1) Pattern solutions of aluminum chloride: approximately 900 mg. of $Cl_3Al.6H_2O$ were weighed and the volume was increased to 100 ml. with HCl 1:20. The concentration was evaluated gravimetrically and adjusted to 1,000 mg of aluminum per ml.

2) Standard aluminum solutions (like chloride): these solutions were prepared using the solution obtained in (1), by diluting it in hydrochloric acid of adequate concentration for every specific case.

3) Aluminum nitrate solution: Approximately 1.4 g of $(NO_3)_3Al.9H_2O$ were weighed and its volume changed to 100 ml. using deionized water. The concentration was adjusted gravimetrically to 1,000 mg. of aluminum per ml.

4) Standard solutions of aluminum (like nitrate): these were prepared by diluting the solution obtained in (3).

5) Pattern solutions of the different ions: these were prepared with the salts, acids or oxides (conveniently dissolved) which will be mentioned in every case, and the drugs were used in the quantities necessary to obtain concentrations of 100 mg. of element per ml. of solution.

6) Standard solutions of the different ions: these were obtained by diluting the above mentioned solutions.

7) 0.1 and 0.01% solutions of CI 202 in deionized water.

8) 0.1% solution of CI 202 in ethyl alcohol.

9) Controlling acetic-acetate solution: 1M in sodium acetate and acetic acid.

10) Hydrochloric acid solutions: obtained by distilling 50% diluted hydrochloric acid at atmospheric pressure in a quartz distillation apparatus.

11) Sodium hydroxide solution with concentration of approximately 40%: The small particles of sodium hydroxide were washed by decantation at atmospheric pressure in a platinum container using deionized water, and were then dissolved in the same container. The solution was diluted using a convenient volume of deionized water.

12) Less concentrated solutions of hydrochloric acid and sodium hydroxide: These were prepared by diluting the solutions described in (10) and (11) respectively.

C. Control of the Instrumental Variables:

While trying to attain our first goal, it was taken into account
that the last step in the analytic process is the measurement of the
fluorescent intensity of the complex formed. These measurements were
carried out using the attachment for spectral fluorescence of the Beckman
spectrometer, model DU, which permits the reading of fluorescent radia-
tion of a definite wave length. This attachment was preferred to that
of total fluorescence because:

a) The tungsten lamp used in the latter is a less powerful exci-
tation source than the mercury lamp used in the spectral fluorescence
attachment, therefore, the values of fluorescence intensity - I_f -
obtained were smaller, decreasing the sensitivity of the method.

b) The possibility of choosing the most convenient wave length to
carry out the measurement could eliminate the potential influence of
fluorescent compounds having different spectrum.

Since the I_f is measured using an arbitrary scale, the values ob-
tained will vary as soon as the response of the measuring instrument is
altered by modifying its sensitivity, the number of diodes connected to
the photomultiplier tube, or the slit width.

The correct handling of these variables leads to good analytic
results and permits to vary the effectiveness of the method according
to the circumstances. Using standard fluorescent glass in the lower
part of the container holder, a series of experiments were performed
to decide under what conditions the measurements of I_f may be carried
out more conveniently.

1) Reproducibility: Once the instrument was set to work it was
observed that the I_f obtained during a relatively long period of time
vary, until they are sensibly different when they become more and more
spaced in time. However, taking into account that each reading requires
approximately 10 to 15 seconds, a series of more than ten standard solu-
tions may be measured without detecting any influence of this factor.
With every series of measurements made in no more than 10 minutes, values
for different fluorescence intensities were obtained.

2) Sensitivity control: The sensitivity of the instrument may
be increased 8 to 9 times by turning the corresponding dial clockwise
from one end to the other [See note]. With the dial in the last posi-
tion maximum sensitivity is obtained. However, the values of I_f obtained
under this condition are not easily reproducible, and it is necessary to
take several readings of every desired intensity. Most of the time it
will be sufficient to set the dial between its midpoint and one or two
turns before attaining maximum sensitivity.

The result is similar to that obtained when measuring flame intensities with this instrument, equipped with the corresponding attachment.

TABLE I

Reproducibility

Serie N°	I_f	Average	ϵ	ϵ^2	$S = \sqrt{\dfrac{\Sigma\epsilon^2}{n-1}}$
1	39.5		0	0	
	39.5		0	0	
	39.4	39.5	0.1	0.01	0.06
	39.5		0	0	
	39.6		0.1	0.01	
	39.5		0	0	
2	10.0		0.03	0.0009	
	10.1		0.07	0.0049	
	10.1	10.03	0.07	0.0049	0.08
	9.9		0.13	0.0169	
	10.0		0.03	0.0009	
	10.1		0.07	0.0049	

3) Response of the photomultiplier tube: The response of this sensible element depends on the number of diodes connected. For the measurement of small luminous intensities, like the ones to be measured, it is convenient to operate at large amplifications, although the fluctuations observed in the galvanometer when all the diodes are connected may require several readings, in order to take an average. (Fig. 1).

By connecting nine diodes, sufficiently stable and reproducible values may be obtained, and a good degree of sensitivity is attained.

4) Slit width: It is necessary to take into account that even using maximum amplification for the responses, it is impossible to measure radiation of very small slit width, because the fluorescence intensities to be measured are relatively weak. However, working with slits of the order of 0.5 mm, it will be possible to measure radiation whose band width for medium intensity is approximately 17 mμ using wave lengths of about 600 mμ, which permits good selectivity. It is convenient to point out that if it is not necessary to eliminate radiations of fluorescent interferences with different spectra, the slit width may increase, since the value of the readings increase as a function of the slit width. (Fig. 2).
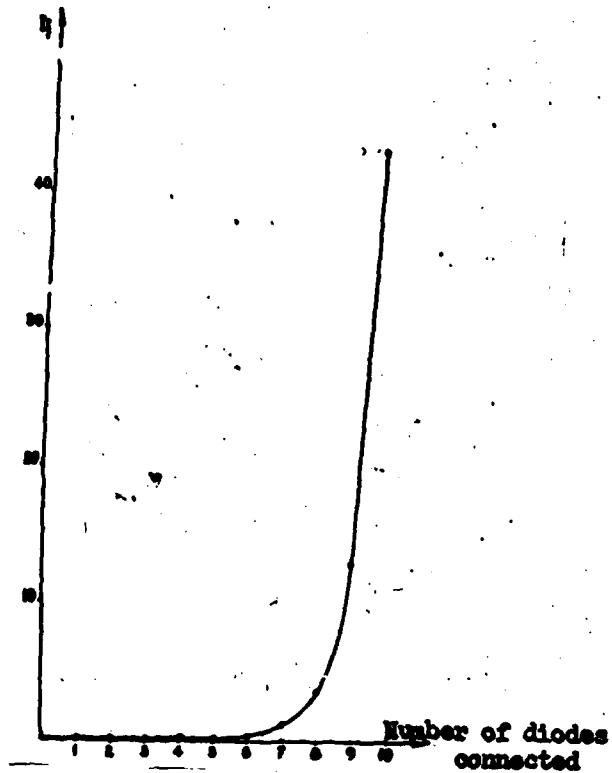
Fig. 1. Response of the photomultiplier tube.
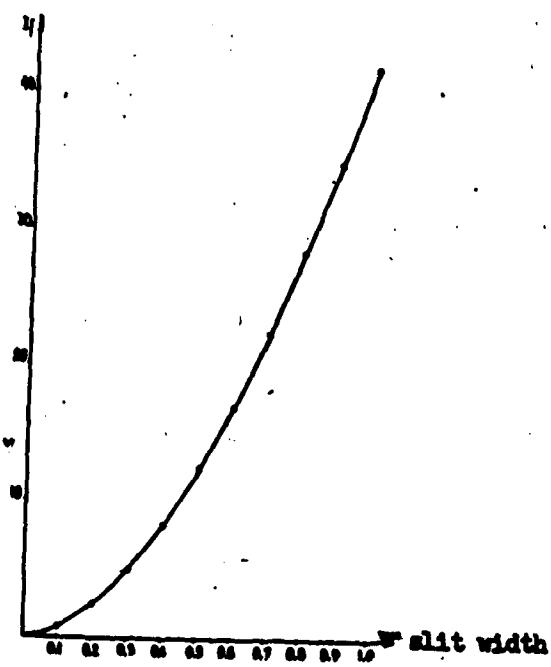
Fig. 2. Influence of the slit width.

D. Absorption and Fluorescence Spectra:

The absorption spectra corresponding to the reagent and to the complex it forms with aluminum were obtained by preparing a white and a standard in the following form: to 15 ml. of the solution - white or standard - 5 ml. of the acetic-acetate solution and 5 ml. of the 0.01% solution of CI 202 in water were added. This was heated in a double boiler, cooled and used for readings in quartz containers with a light path of 10,000 mm. From 220 up to 450 mμ a hydrogen lamp was used, and for longer wave lengths a tungsten filament was used. The slit width was kept sufficiently small to operate with beams of band width no greater than 1 mμ at medium intensity. (Fig. 3).
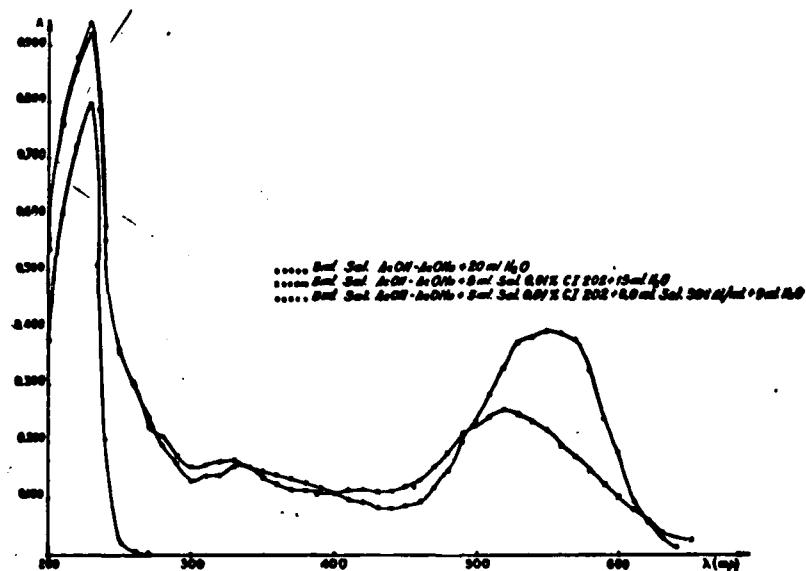
Fig. 3. Absorption spectra.

It can be observed that the peaks of maximum absorption in the visible range occur at 520 mμ for the coloring agent in deionized water and at 560 mμ for the complex it forms with aluminum, using the same solvent.

The peak of maximum absorption in samples with excess of coloring agent will depend on the relation complex concentration/coloring agent.

Operating with excess of coloring agent and using a wave length of 560 mμ, it would be ssible to make an absorbchrometric evaluation of aluminum with a sensitivity of the order of 0.01 γ of Al/cm^2 /See note/. Both the white and the standard absorb strongly any radiation of wave length smaller than 240 mμ. (Fig. 4).

- 9 -

The possible variation in the sensitivity of the photo-multiplier tube at different wave lengths was not considered.
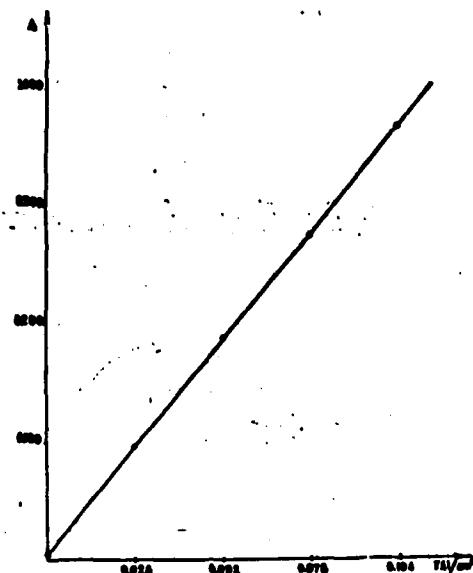
Fig. 4. Curve of absorptiometric evaluation of aluminum.

The fluorescence spectra of deionized water, a white solution and a standard solution prepared in the same way were then obtained. In all three cases quartz containers were used, and the samples were irradiated using a mercury lamp No. 2260 with a Corning 9863 filter. This filter permits the passage of radiation of wave length from 230 mμ to 420 mμ. (Fig. 5).

From the study of these spectra it can be concluded that the wave length corresponding to maximum (apparent) fluorescence [See note] of the aluminum complex is 605 mμ. This value depends somehow on the slit width used, since the maximum of I_f is displaced toward the longer wave length region and the curve becomes relatively flat as the slit width increases. Of course, the displacement of the maximum is due to the fact that the spectrum is not perfectly symmetric with respect to the maximum of I_f. (Fig. 6).

[Note:] Applying the technique indicated in F. this value may reach 0.005 γ Al/cm^2.

- 10 -
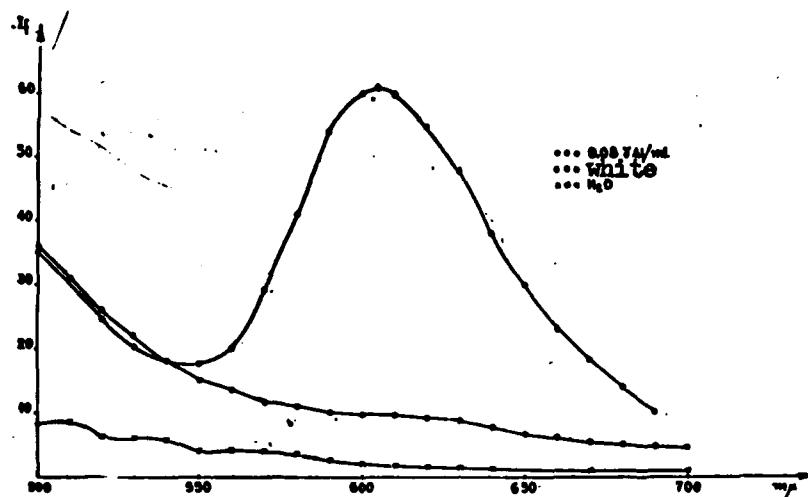
Fig. 5. Fluorescence spectra of deionized water, CI 202 and aluminum complex.
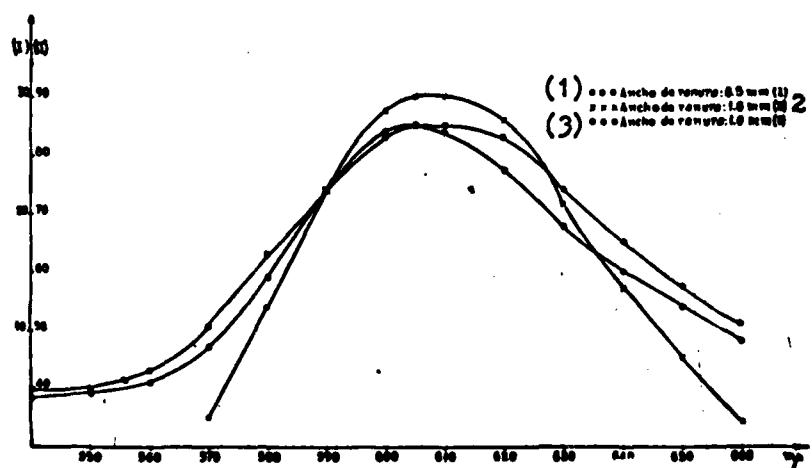
Fig. 6. Influence of slit width on the fluorescence spectrum.

Legend: 1 - slit width: 0.5 mm (1)
2 - slit width: 1.0 mm (II)
3 - slit width: 1.0 mm (I)

- 11 -

E. Study of the Variables of the Analytic Process:

The study and control of the chemical process variables which affect the analytical results is fundamental, and therefore it is our next objective once the optimum wave length for the measurement of fluorescence has been determined. The necessary experiments for the study of every variable were performed keeping the working conditions of the instrument constant, to obtain comparable values.

1) Influence of time in the development of fluorescence. It is well known that the formation of the fluorescent compound is not instantaneous. Therefore, the time required to attain maximum development of fluorescence was determined. The values shown in Table II were obtained by reading fractions of two solutions -- white and standard -- for 48 hours, from the moment volume and homogenization were attained. From this table it can be concluded that to achieve total development at room temperature, about 48 hours are required.

TABLE II

Influence of Time in the Development of Fluorescence

Time	I_f White	I_f 0.2 γ Al/ml
1 minute	2.5	4.5
5 minutes	3.0	7.0
10 "	3.2	8.2
15 "	3.1	12.1
20 "	3.0	14.4
30 "	3.1	17.3
60 "	3.2	23.5
24 hours	4.0	46.2
48 "	5.2	52.3
72 "	5.0	52.0

2) Influence of heating time in a double boiler: White and standard solutions were prepared using 0.4 γ Al/ml, and the time of heating in a double boiler was varied. They were cooled in ice water at the end of the heating periods, and the series was read at the end of the experiment. As a result of this, it can be established that a heating time of 10 minutes in a double boiler is enough for the total development of fluorescence.

TABLE III

Influence of the Heating Time

Time (minutes)	I White	I_f Standard (0.4 γ Al/ml)
1	4.0	45.5
5	4.5	52.5
10	5.0	55.5
15	5.0	55.0
20	4.5	54.0

TABLE IV

Influence of pH

Standard No.	Al γ/ml	pH	I_f	ΔI_f
1	0	2.7	10.4	—
2	0.08	2.7	20.0	9.6
3	0	3.8	13.0	—
4	0.08	3.8	41.0	28.0
5	0	4.3	13.0	—
6	0.08	4.3	45.5	32.5
7	0	4.7	13.0	—
8	0.08	4.7	44.5	31.5
9	0	5.0	12.8	—
10	0.08	5.0	44.0	31.2
11	0	5.9	11.0	—
12	0.08	5.9	26.0	15.0

3) Influence of pH: The necessity to operate with a controlled pH is mentioned several times in the bibliography, and 4.5[2] or 4.8[3] are indicated as maximum values. Experiments were performed and their results are shown in Table IV. White and standard solutions with 0.08 γ Al/ml were prepared in the following way: to a volume of solution convenient for the experiment -- approximately 5 ml -- 5.0 ml of the controlling acetic acetate solution and 5.0 ml. of the 0.01% coloring agent solution were added. To each white and standard solution a convenient volume of approximately 4N sodium hydroxide or hydrochloric acid solution was added to obtain the indicated pH. The volume was changed to 25 ml

with deionized water and the solution obtained was homogenized and heated
in a double boiler for 10 minutes. It was then cooled to room tempera-
ture using ice water and the I_f's of the series were read using a wave
length of 605 mμ. From the study of the values of ΔI_f at different pH's
it seems to be convenient to perform the experiment at pH 4.3. It must
be mentioned that when the pH increases, the coloring agent turns to
blue-violet and it is destroyed in a completely alkaline medium. This
process is accelerated when the solutions are heated.
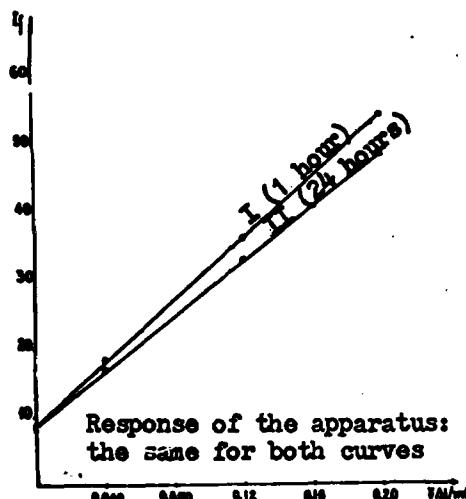
Fig. 7. Stability of fluorescence as a function of time.

4) Fluorescence stability control: A series of readings of sev-
eral solutions were made, and the values observed in Fig. 7 were obtained.
It can be seen that greater differences are produced as the aluminum con-
centration increases. Anyway, since the proportionality between concen-
tration and fluorescent intensity is maintained, the small instability of
I_f does not prevent the reading of correct values if the standard solu-
tions and the samples are read simultaneously. (Fig. 7).

5) Effects of radiation: A white solution and a standard solu-
tion containing 0.04 γ of aluminum per ml. were irradiated during longer
and longer periods of time. The results obtained show that in the time
necessary to take three or four readings of the same solution, no more
than a minute, no decrease in I_f is observed. The effect of a longer
exposure time seems to become more important, but the observed decrease
in I_f may be due to an increase in temperature, since the same standard
solution heated, but not irradiated, showed smaller values of I_f (ΔT =
8°C).

TABLE V

Influence of the Irradiation Time

Irradiation time	I_f	
	White	0.4 γ Al/ml.
10 sec.	5.5	42.1
1 min.	5.5	42.0
5 min.	5.6	41.5
10 "	5.5	41.0

6) Stability of the coloring solution: It was considered conven-
ient to control the influence of time in the CI 202 solution. For this
purpose white and standard solutions of the same concentration were pre-
pared, and for every white-standard pair reagent solutions prepared on
different days and preserved differently were used. From the values ob-
tained it can be concluded that:

a) the solution gets old, yielding smaller values of I_f as time
goes on.

b) this process is slowed down if the solution is preserved away
from light and in a refrigerator.

TABLE VI

Influence of Time in the Coloring Solution

Series	No.	Age of the CI 202 solution	Preservation	I_f		
				White	0.08 γ Al/ml	0.4 γ Al/ml
1 (*)	1	1 hour	At room temperature, exposed to light	7.5	-	56.0
	2	1 day		7.5	-	55.5
	3	1 month		7.0	-	40.0
	4	2 months		6.0	-	26.5
	5	5 months		5.5	-	14.0
2 (*)	1	1 hour	In refriger-ator, shielded from light	10.0	32.0	-
	2	1 day		9.9	32.0	-
	3	1 month		9.8	30.1	-
	4	2 months		9.5	28.0	-

(*) Series (1) and (2) were obtained separately and with the
instrument set for different sensitivity.

7) Influence of the solvent and of the concentration of the CI 202 solution: White and standard solutions of equal concentration were prepared, the CI 202 solutions were prepared as follows:

i) 0.01% in deionized water.

ii) 0.1% in deionized water.

iii) 0.1% in 95° ethyl alcohol.

In the three cases the results obtained were similar. However, the 0.01% aqueous solution was preferred because:

a) The error in the amount of coloring added is smaller, therefore, the results obtained are less dispersed.

b) When the standard solutions prepared using the CI 202 alcoholic solution are heated in a double boiler, they boil, which may cause the production of projections.

8) Reproducibility: Repeating the operation five times it was proved that the I_f produced by white and standard solutions obtained simultaneously are reproducible. The standard deviation expressed in γ Al/ml. is 0.0001 for concentrations of the order of 0.040 γ of aluminum per ml. It must be pointed out that in this case the experiment was not performed using the maximum sensitivity of the apparatus.

TABLE VII

Reproducibility in the Evaluation of Al

N°	Al (γ/ml.)	I_f	Average	ϵ	ϵ^2	S
1	0	20.0		0	0	
2	0	20.1		+ 0.10	0.01	
3	0	19.9	20.00	— 0.10	0.01	0.07
4	0	20.0		0	0	
5	0	20.0		0	0	
6	0.040	60.1		+ 0.12	0.0144	
7	0.040	59.8	59.98	— 0.18	0.0324	
8	0.040	60.0		+ 0.02	0.0004	0.13
9	0.040	60.1		+ 0.12	0.0144	
10	0.040	59.9		— 0.08	0.0004	

F. Calibration Curves:

Taking into account our conclusions from parts D and E, the details for the procedure to be followed in the evaluation of aluminum with CI 202 were established. Besides, with the instrumental possibilities studied in part C, it was possible to operate in different ranges of concentration of the element under study.

Technique used: To the solution to be evaluated (usually no more than 10 ml.) 5.0 ml. of acetic-acetate controlling solution and 5.0 ml. of 0.01% CI 202 solution in deionized water are added (if it is necessary, the pH is adjusted to 4.3 using a solution of sodium hydroxide or hydrochloric acid with a convenient concentration). The volume is changed to 25 ml. This solution is homogenized and heated in a double boiler for ten minutes. It is then cooled to room temperature in ice water and the If is then read using a wave length of 605 mμ. White and standard solutions must be handled simultaneously.

CONDITIONS
Diodes connected: 9
Slit width: 0.5 mm
Sensitivity: maximum
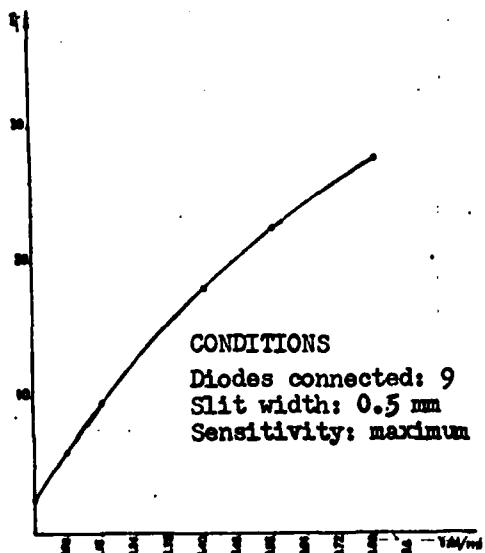
Fig. 8. Calibration curve for concentrations of 0.04-0.08 γ of Al/ml.

CONDITIONS
Diodes connected: 10
Slit width: 0.2 mm
Sensitivity: 1 turn before the max.
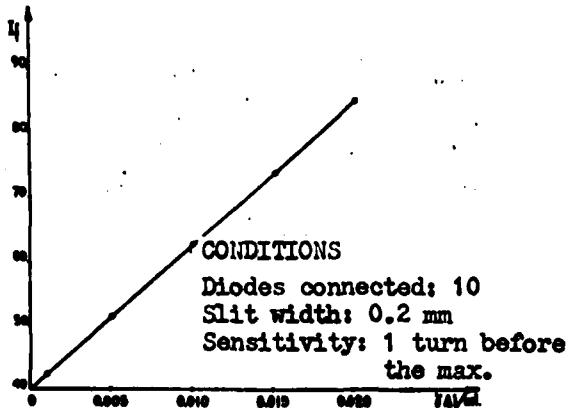
Fig. 9. Calibration curve for low concentrations of aluminum.

The readings obtained using white and standard solutions with increasing concentrations of aluminum may be seen in Figs. 8 /see note/ and 9.

/Note:/ During the processing of the white and standard solutions corresponding to this curve, 10 ml. of 0.01% CI 202 solution in water were added.

- 17 -

From these figures it can be concluded that:

1) The relation I_f/aluminum concentration stops being linear when the aluminum concentration is increased. Anyway, it stands to reason that the curve may be used for the evaluation of aluminum, because even when the slope decreases as the concentration of the fluorescent compound increases, the relative error in the determination decreases.

2) The sensitivity obtained under the operating conditions used to obtain the curve shown in Fig. 9 is 0.0001 γ of Al/ml.

3) When working in the linear portion of the graph, it will be enough to process a known standard solution together with the sample and interpolate or extrapolate the result.

G. Influence of Strange Ions:

The discrepancy observed in the bibliography related to the ions which would interfere in the evaluation of aluminum with CI 202 makes a new study of this problem necessary. The results obtained after studying the influence of several ions are shown in Table VIII. In every case, white and standard solutions with concentration of 0.04 γ of aluminum per ml., with and without the ion under study, were processed using the technique described in F.

All the experiments were repeated three times. In some cases slightly and equally increased values are observed in white and standard solutions where the concentration of the interfering ion was increased. If at the same time no variation was observed in the solutions, this could be due to the presence of small quantities of aluminum in the drugs used. It is convenient to remember that any experiment involving the use of acid solutions was done in quartz containers to avoid contamination due to the aluminum present in glass.

From Table VIII it may be concluded that at least up to the concentrations used in the experiments, the following ions do not interfere: Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}, BO_3^{3-}, Tl^+, SiO_3^{2-}, Pb^{++}, NO_3^-, PO_4^{3-}, AsO_4^{3-}, SO_4^{2-}, SO_3^{2-}, SeO_4^{2-}, SeO_3^{2-}, Cl^-, Br^-, I^-.

On the other hand, Sc^{3+}, Y^{3+}, La^{3+}, Mn^{++}, Ni^{++}, Zn^{++}, Hg^{++}, In^{3+}, Sb^{3+}, and most of the rare earth elements in the table interfere slightly, and their presence can be tolerated when the concentration is small (of the order of 4 γ per ml., which would yield aluminum/interference ratios of the order of 1:1000 or even better in some instances, with less than 5% error).

However, the other ions checked interfere considerably, and therefore should not be present. (See Table VIII, page 19 and following.)

TABLE VIII

Element	Ion added	Drugs used	Al/element ratio	Effect on I_f in γ of Al/ml	Observations
Li	Li +	$SO_4Li_2 \cdot H_2O$ p.a.	0: 1.000 1: 1.000	+ 0.001 + 0.041	Does not interfere
Na	Na +	ClNa p.a.	0: 50.000 1: 50.000	+ 0.001 + 0.041	Idem
K	K +	ClK p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Rb	Rb +	ClRb p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Cs	Cs +	ClCs p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Be	Be ++	$SO_4Be \cdot 4H_2O$ p.a.	0: 1.000 1: 1.000	0.000 + 0.040	Idem
Mg	Mg ++	$(AcO)_2Mg \cdot 4H_2O$ p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Ca	Ca ++	Cl_2Ca p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Sr	Sr ++	$Cl_2Sr \cdot 6H_2O$ p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem
Ba	Ba ++	$Cl_2Ba \cdot 2H_2O$ p.a.	0: 5.000 1: 5.000	0.000 + 0.040	Idem

TABLE VIII (continued)

Element	Ion added	Drugs used	Al/element ratio	Effect on If in γ of Al/ml	Observations
Sc	Sc+++	Sc₂O₃ s.p. ClH p.a. dest.	0: 500 / 1: 500	+0.002 / +0.043	Interferes slightly
Y	Y+++	Cl₃? p.a.	0: 1.000 / 1: 1.000	+0.005 / +0.044	Idem
La	La+++	La₂O₃ s.p. Cl H p.a. dest.	0: 1.000 / 1: 1.000	+0.005 / +0.045	Idem
Ti	Ti++++	Ti' s.p. SO₄H₂ p.a. dest	0: 500 / 1: 500	— / —	Flaky gray-green precipitate
Zr	ZrO.++	ZrOCl₂·8H₂O p.a.	0: 500 / 1: 500	−0.013 / −0.004	Violet color; stops fluorescence, slight hydrolysis
V	VO₃⁻	VO₃Na·4H₂O p.a.	0: 200 / 1: 200	−0.014 / −0.014	Stops fluorescence
Nb	Nb⁵+	Cl₅Nb p.a.	0: 150 / 1: 150	−0.003 / +0.014	Turbidness due to hydrolysis, stops fluorescence
Cr	CrO₄=	CrO₄K₂ p.a.	0: 200 / 1: 200	— / —	Destroys the coloring agent
	Cr+++	(AcO)₃Cr·H₂O p.a.	0: 500 / 1: 500	−0.004 / +0.027	Blue-violet color, stops fluorescence partially
Mo	MoO₄=	Mo₇O₂₄(NH₄)₆·4H₂O p.a.	0: 200 / 1: 200	−0.002 / +0.030	Red-violet color, stops fluorescence partially
W	WO₄=	WO₄H₂ p.a. OHNa p.a. purif.	0: 200 / 1: 200	−0.005 / +0.035	Less orange color; stops fluorescence partially

TABLE VIII (continued)

Element	Ion added	Drugs used	Al/element ratio		Effect on I_f in γ of Al/ml	Observations
Mn	MnO₄ -	MnO₄K p.a.	0: 200	1: 200	— —	MnO2 precipitate destroys the coloring agent
	Mn++	SO₄Mn · 4H₂O p.a.	0: 200	1: 200	+ 0.001 + 0.041	Lighter color as the Mn++ concentration increases
			0: 500	:1 500	+ 0.004 + 0.046	
			0: 1.000	1: 1.000	+ 0.009 + 0.053	
Fe	Fe +++	(SO₄)₂Fe(NH₄) 12H₂O p.a.	0: 100	1: 100	— —	Iron hydrolysis
	Fe++	Cl₂Fe p.a.	0: 500	1: 500	— 0.009 — 0.006	Stops the reaction; brownish color (partially turns to Fe+++)
Co	Co++	Cl₂Co · 6H₂O p.a.	0: 200	1: 200	— 0.013 — 0.013	Lavender color. Stops fluorescence
Ni	Ni++	Cl₂Ni · 6H₂O p.a.	0: 200	1: 200	— 0.001 + 0.038	Does not interfere too much
Ru	Ru +++	Cl₃Ru p.a.	0: 1.000	1: 1.000	— 0.009 + 0.011	More reddish color; stops fluorescence appreciably
		Cl₃Ru p.a.	0: 880	1: 880	— 0.010 — 0.010	Light brown color; stops fluorescence
Rh	Rh +++	Cl₃Rh p.a.	0: 1.000	1: 1.000	— 0.012 — 0.004	More orange color; stops fluorescence

TABLE VIII (continued)

Element	Ion added	Drugs used	Al/element ratio	Effect on If in γ of Al/ml	Observations
Pt	Pt ++++	Pt° s.p. ClH p.a. dest. NO₃H p.a. dest.	0: 900 1: 900	−0.027 −0.027	Destroys the coloring agent
Cu	Cu ++	Cl₂Cu · 2 H₂O p.a.	0: 200 1: 200	−0.011 −0.011	Stops fluorescence
Ag	Ag +	Ag° s.p. NO₃H p.a. dest.	0: 1.000 1: 1.000	−0.001 + 0.026	Destroys the coloring agent (Cl Ag pp. if there are small quantities of Cl⁻ in the CI 202)
Au	Au +++	Au° s.p. ClH p.a. dest. NO₃ H p.a. dest.	0: 1.000 1: 1.000	— —	Destroys the coloring agent forming Au precipitate
Zn	Zn ++	SO₄Zn · 7 H₂O p.a.	0: 500 1: 500	+ 0.003 + 0.044	Interferes slightly
			0: 1.000 1: 1.000	+ 0.009 + 0.054	
Cd	Cd ++	CdO p.a. ClH p.a. dest.	0: 1.000 1: 1.000	0.000 + 0.040	Does not interfere
Hg	Hg ++	Hg° redest. NO₃H p.a. dest.	0: 500 1: 500	+ 0.002 + 0.043	Makes the solution take a lighter color
			0: 1.000 1: 1.000	− 0.002 + 0.036	Stops fluorescence partially
B	BO₃ ≡	BO₃H₃ p.a.	0: 1.000 1: 1.000	+ 0.001 + 0.040	Does not interfere
Ga	Ga +++	Ga₂O₃ s.p. ClH p.a. dest.	0: 20 1: 20	+ 0.047 + 0.079	Interferes because of the fluorescence of the Ga compound with the violet colored CI 202

TABLE VIII (continued)

Element	Ion added	Drugs used	Al/element ratio	Effect in I$_f$ in γ of Al/ml	Observations
In	In +++	In$_2$O$_3$ s. p. ClH p.a. dest.	0: 1.000 1: 1.000	+ 0.007 + 0.047	More violet color. Interferes slightly
Tl	Tl +	NO$_3$Tl p.a.	0: 1.000 1: 1.000	0.000 + 0.040	Does not interfere
Si	SiO$_3$=	SiO$_2$ p.a. OHNa p.a. purif.	0: 1.000 1: 1.000	0.000 + 0.040	Idem
Sn	Sn ++	Cl$_2$Sn p.a. ClH p.a. dest.	0: 500 1: 500	− 0.015 − 0.013	Slight turbidness. Stops fluorescence
Pb	Pb ++	(NO$_3$)$_2$Pb p.a.	0: 1.000 1: 1.000	+ 0.003 + 0.043	Less orange color
N	NO$_3$ −	NO$_2$Na p.a	0: 2.000 1: 2.000	0.000 + 0.040	Does not interfere
	NO$_2$ −	NO$_3$Na p.a.	0: 100 1: 100	− 0.010 − 0.010	Destroys the coloring agent
P	PO$_4$ ≡	PO$_4$H(NH$_4$)$_2$ p.a.	0: 1.000 1: 1.000	0.000 + 0.040	Does not interfere
As	AsO$_4$ =	A$_2$O$_4$HNa$_2$ · 7 H$_2$O p.a.	0: 1.000 1: 1.000	0.000 + 0.040	Idem
Sb	Sb +++	Cl$_3$Sb p.a. ClH p.a. dest.	0: 500 1: 500	+ 0.002 + 0.044	Interferes slightly
			0: −1.000 1: 1.000	+ 0.006 + 0.047	Interferes slightly

TABLE VIII (continued)

Element	Ion added	Drugs used	Al/element ratio	Effect on If in γ of Al/ml	Observations
Bi	Bi +++	Bi₂O₃ p.a. ClH p.a. dest.	0: 2.00 1: 200	−0.002 +0.036	More violet color; stops fluorescence partially
			0: 500 1: 500	−0.003 +0.030	Does not precipitate
S	SO₄ =	SO₄Na₂ 10 H₂O p.a.	0: 1.000 1: 1.000	(—)	Precipitates by hydrolysis
	SO₃ =	SO₃Na₂ p.a.	0: 1.000 1: 1.000	0.000 +0.040	Does not interfere
Se	SeO₄ =	SeO₄Na₂ p.a.	0: 1.000 1: 1.000	−0.001 +0.039	Idem
	SeO₃ =	SeO₃Na₂ p.a.	0: 1.000 1: 1.000	+0.001 +0.041	Idem
F	F −	F(NH₄) p.a.	0: 100 1: 100	−0.018 −0.007	Stops fluorescence (forming a complex with Al⁺⁺⁺)
Cl	Cl −	ClK p.a.	0: 5.000 1: 5.000	0.000 +0.040	Does not interfere
Br	Br −	BrNa p.a.	0: 1.000 1: 1.000	0.000 +0.041	Idem
I	I −	IK p.a.	0: 1.000 1: 1.000	0.000 +0.040	Idem
Ce	Ce ++++	(SO₄)₂Ce p.a. SO₄H₂ p.a. dest.	0: 500 1: 500	−0.017 −0.017	Destroys the coloring agent
	Ce +++	(SO₄)₂Ce p.a. SO₃Na₂ p.a.	0: 200 1: 200	+0.006 +0.046	Interferes fairly

			0:/1:		±	
			0:			
			1:		0.043	
			0:			
			1:		0.042	
Tb	Tb +++	Tb₂O₃ s.p. CIII p.a. dest.	0:	500	0.003	Idea
			1:	500	0.043	
Dy	Dy +++	Dy₂O₃ s.p. CIII p.a. dest.	0:	500	0.004	Idea
			1:	500	0.044	
Er	Er +++	Er₂O₃ s.p. CIII p.a. dest.	0:	500	0.001	Idea
			1:	500	0.016	
Tm	Tm +++	Tm₂O₄ s.p. CIII p.a. dest.	0:	300	+0.003	Idea
			1:	300	+0.043	
Yb	Yb +++	Yb₂O₃ s.p. CIII p.a. dest.	0:	500	+0.003	Idea
			1:	500	+0.013	
Lu	Lu +++	Lu₂O₃ s.p. CIII p.a. dest.	0:	500	+0.002	Idea
			1:	500	+0.013	
U	UO₂ ++	U₃O₈ p.a. NO₃H p.a. dest.	0:	500	−0.001	more violet color. Steps fluorescence peculiarity
			1:	500	+0.031	
			0:	1.000	−0.002	
			1:	1.000	+0.027	
Th	Th ++++	(NO₃)₄ Th 6 H₂O	0:	500	+0.009	Less orange-red color
			1:	500	+0.033	

CONCLUSIONS

1. The operating conditions of the Beckman spectrophotometer, model DU with attachment for the determination of spectral fluorescence were studied in order to determine its possibilities and limitations. It was concluded that:

   a) In most of the cases it is convenient to adjust the sensitivity of the instrument between the midpoint and one turn before reaching the maximum sensitivity of the corresponding potentiometer.

   b) It is convenient to connect up to 9 diodes of the photomultiplier tube, leaving the tenth position for cases of extremely low concentrations.

   c) It is possible to operate with a slit width between 0.2 and 1.0 mm, according to the aluminum concentration and to the sample composition.

2. The absorption spectra of the reagent and the compound it forms with aluminum in deionized water were obtained. These spectra exhibit maxima at 520 and 560 mμ respectively. We accept as possible the absorptiometric evaluation of aluminum operating against the reagent at a wave length of 560 mμ (a sensitivity of the order of 0.005 γ Al/cm^2 could be obtained using the proposed technique).

3. From the fluorescence spectra of deionized water, a white, and a standard solution, the optimum wave length for the evaluation of the fluorescent complex was established to be 605 mμ.

4. The variables affecting the values of I_f obtained were studied, and working techniques were developed.

5. It was shown that the I_f varies linearly with the aluminum concentration when this one is maintained under 0.2 γ of aluminum/ml. For larger concentrations, the calibration curves obtained permit a correct evaluation of aluminum concentration. When operating under adequate conditions it is possible to attain a sensitivity of 0.0001 γ Al/ml.

6. The influence of most of the ions potentially present in a sample in highly unfavorable concentrations was controlled, and it was concluded that:

   a) Up to concentrations of 40 γ/ml the following ions do not interfere: Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cd^{++}, BO_3^{3-}, Tl^+, SiO_3^{2-}, Pb^{++}, NO_3^-, PO_4^{3-}, AsO_4^{3-}, SO_4^{2-}, SO_3^{2-}, SeO_4^{2-}, SeO_3^{2-}, Cl^-, Br^-, I^-.

b) The following ions interfere slightly, therefore their presence can be tolerated in concentrations up to 4 γ/ml: Sc^{3+}, Y^{3+}, La^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, In^{2+}, Sb^{3+}, and most of the rare earth elements which were tried.

c) The following ions interfere seriously and should not be present: Ti^{4+}, ZrO^{++}, VO_3^-, Nb^{5+}, CrO_4^{2-}, Cr^{3+}, MoO_4^{2-}, WO_4^{2-}, MnO_4^-, Fe^{3+}, Fe^{2+}, Co^{++}, Ru^{3+}, Rh^{3+}, Pt^{4+}, Cu^{++}, Ag^+, Au^{3+}, Ga^{3+}, Sn^{++}, NO_2^-, Bi^{3+}, F^-, Ce^{4+}, Ce^{3+}, UO_2^{2+}, Th^{4+}.

BIBLIOGRAPHY

1. White, C. and Lowe, C.: Ind. Eng. Chem., Anal. Ed. 9, 430 (1937).

2. Bourstyn, M.: Mull. Soc. Chim., 8, 540 (1941).

3. Weissler, A. and White, C.: Ind. Eng. Chem., Anal. Ed., 18, 530 (1946).

4. Charlot, G.: Anal. Chim. Acta 1, 218 (1947).

5. Ishibashi, M.; Shigematsu, T. and Nishikawa, Y.: Bunseki Kagaku, 6, 568 (1957).

6. Possidoni de Albinati, Julia Flavia: Anales de la Asociacion Quim. Argentina, 43, 106 (1955).

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